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Grant or Contract N00014-89-J-1590

R&T Code 413m012

Technical Report No. 3

Polymerization of Nitro Compounds on Silver Surfaces
During Surface-Enhanced Raman Scattering

by

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Prepared for Publication

in

Journal of Raman Spectroscopy

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December 1, 1989

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION None			1b. RESTRICTIVE MARKINGS None		
2a. SECURITY CLASSIFICATION AUTHORITY None			3. DISTRIBUTION/AVAILABILITY OF REPORT This document has been approved for public release and sale; its distribution is unlimited.		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE None					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #3			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Cincinnati		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Department of Materials Science Cincinnati, OH 45221-0012			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-89-J-1590		
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Polymerization of Nitro Compounds on Silver Surfaces During Surface-Enhanced Raman Scattering					
12. PERSONAL AUTHOR(S) W. H. Tsai, F. J. Boerio, S. J. Clarson, and G. Montaudo					
13a. TYPE OF REPORT Technical Report		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) December 1, 1989	
				15. PAGE COUNT 35	
16. SUPPLEMENTARY NOTATION Prepared for publication in the Journal of Raman Spectroscopy					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Surface-Enhanced Raman Scattering, Nitro Compounds, Polymerization		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Surface-enhanced Raman scattering was observed from thin films formed by 1,4- and 1,3-dinitrobenzene spin-coated onto silver island films from dilute solutions. During laser irradiation of 1,4-DNB films on silver substrates at relatively high laser powers, new bands appeared near 1152, 1350, 1412, and 1460 cm^{-1} and bands near 1118, 1358, and 1372 cm^{-1} decreased in intensity. A band near 1598 cm^{-1} shifted to near 1605 cm^{-1} . The bands near 1152 and 1412 cm^{-1} were assigned to stretching modes of C-N and -N=N- bonds of azo compounds, respectively, indicating that polymerization of 1,4-DNB had occurred. The extent of polymerization was greatest when the surface coverage of adsorbed 1,4-DNB was greatest and when the SERS experiments were carried out in a nitrogen atmosphere, indicating that reducing conditions were required for the polymerization. No polymerization was observed for 1,3-DNB under similar circumstances. The difference was attributed to orientation of the adsorbed species. Thus, it was concluded that 1,4-DNB was adsorbed with a horizontal configuration in which the aromatic rings were parallel to the substrate surface.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Joann Milliken			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

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August 31, 1989

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
Distribution	
Availability Codes	
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Abstract

Surface-enhanced Raman scattering was observed from thin films formed by 1,4- and 1,3-dinitrobenzene spin-coated onto silver island films from dilute solutions. During laser irradiation of 1,4-DNB films on silver substrates at relatively high laser powers, new bands appeared near 1152, 1350, 1412, and 1460 cm^{-1} and bands near 1118, 1358, and 1372 cm^{-1} decreased in intensity. A band near 1598 cm^{-1} shifted to near 1605 cm^{-1} . The bands near 1152 and 1412 cm^{-1} were assigned to stretching modes of ϕ -N and -N=N- bonds of azo compounds, respectively, indicating that polymerization of 1,4-DNB had occurred. The extent of polymerization was greatest when the surface coverage of adsorbed 1,4-DNB was greatest and when the SERS experiments were carried out in a nitrogen atmosphere, indicating that reducing conditions were required for the polymerization. No polymerization was observed for 1,3-DNB under similar circumstances. The difference was attributed to orientation of the adsorbed species. Thus, it was concluded that 1,4-DNB was adsorbed with a horizontal configuration in which the aromatic rings were parallel to the substrate surface and both nitro groups were in contact with the surface while 1,3-DNB was adsorbed with a vertical configuration in which the rings were perpendicular to the surface and only one nitro group was in contact with the surface.

I. Introduction

Surface-enhanced Raman scattering (SERS) was first observed from pyridine adsorbed onto electrochemically roughened silver electrodes (1). Since then, there has been a great deal of interest in SERS. Numerous theoretical investigations have been directed toward elucidating the mechanisms responsible for SERS, but it now appears that most SERS is related to two mechanisms. One is associated with a long-range electromagnetic resonance within metallic substrates which enhances the electric field at the surface (2). The other is attributed to distortions of the polarizability of the adsorbed molecules by formation of charge-transfer complexes with the metal surface (2). This short-range enhancement reflects the chemical interaction of the adsorbate with the metal surface.

Several papers have appeared describing chemical reactions occurring at the silver surface during SERS experiments. Dorain and co-workers investigated SERS from finely divided silver powder exposed to SO_2 gas in a helium atmosphere and reported the observation of sulfite (SO_3^{2-}) and sulfate ions (SO_4^{2-}) formed catalytically on the silver surfaces (3). After the silver powder was exposed to SO_2 gas for about 2 minutes at room temperature along with the continuous flow of helium gas, two new bands were observed near 615 and 925 cm^{-1} , which were assigned to adsorbed SO_3^{2-} species. This assignment was confirmed when bands were observed near the same frequencies in the normal Raman spectrum of Ag_2SO_3 . Moreover, a new band associated with SO_4^{2-} formed by oxidation of SO_3^{2-} was observed near 962 cm^{-1} when

silver powder that had been exposed to SO_2 was illuminated at much higher intensity (e.g., 500 mW) for ten seconds in an oxygen-containing atmosphere. This assignment was also confirmed when a band was observed near the same frequency in the normal Raman spectrum of Ag_2SO_4 .

Oxidation of sulfite ions to sulfate ions during intense laser irradiation was also observed by Boerio et al (4). In their SERS experiments, glass substrates that were used to support silver island films were cleaned in a mixture of chromic and sulfuric acids, rinsed in distilled water, and dried before being placed in a vacuum chamber for the silver deposition. Residual sulfate ions on the glass were adsorbed onto the silver surface during the silver deposition and reduced to sulfite ions during subsequent laser irradiation. As a result, two bands related to sulfite ions were observed near 640 and 940 cm^{-1} in the SERS spectra obtained at relatively low laser powers (e.g., 100 mW). When the laser power was increased to 200 mW, a band gradually appeared near 960 cm^{-1} due to oxidation of the sulfite ions to sulfate ions.

Dorain and co-workers also investigated SERS from silver powder exposed to NO or $\text{NO}_2/\text{N}_2\text{O}_4$ gas (5). Bands near 245, 815, and 1285 cm^{-1} due to NO_2^- and a band near 1045 cm^{-1} due to NO_3^- were observed. These assignments were confirmed by an investigation of SERS from a Ag electrode immersed in 0.1M KNO_2 electrolyte and normal Raman scattering from AgNO_3 crystals.

Wokaun and Baiker explored the application of SERS for the in-situ characterization of catalytic reactions (6). Results

from SERS indicated that they successfully studied amination reactions of aliphatic alcohols on copper substrates. SERS provided information concerning the reaction mechanism which complemented the evidence from kinetic and chemical determinations in their studies.

Suh and Michaelian investigated polymerization on silver colloid surfaces during SERS. They reported SERS from acrylamide and polyacrylamide adsorbed onto silver colloid particles (7). It was found that the CH_2 stretching modes of acrylamide adsorbed onto silver colloid particles were near 2926 and 2972 cm^{-1} , which corresponded closely to their positions in polyacrylamide but was considerably different from their positions near 3050 and 3115 cm^{-1} for acrylamide in aqueous solutions. There existed, however, differences between SERS spectra of polyacrylamide adsorbed onto silver colloid particles and acrylamide polymerized on silver colloidal surfaces. These differences were attributed to the surface geometry of the two polymers and the existence of non-polymerized species in the adsorbed acrylamide.

Suh et al also reported SERS from acrylic acid adsorbed onto silver colloid surfaces and concluded that polymerization occurred at the silver surface during SERS (8). The evidence supporting this conclusion was that a band near 2928 cm^{-1} associated with the CH_2 stretching mode of the polymer and a band near 1348 cm^{-1} concerning the CH_2 wagging of polymer were observed in the SERS spectra. Suh et al investigated the concentration effect on polymerization during SERS and concluded that polymerization took

place only at low coverages when acrylic acid on the surface was under the flat down geometry.

Boerio et al investigated SERS from thin films of poly (4-methylstyrene), poly (4-chlorostyrene), poly (4-bromostyrene), and poly (4-fluorostyrene) adsorbed onto silver island films (9). They found that the kinetics of polystyrene oxidation were strongly dependent on substituent effects. Following the primary oxidation of polystyrenes by the Norrish Type II reaction, electron-donating substituents of polystyrenes such as F, Cl, Br, and CH_3 accelerated the rate of Norrish Type I reaction causing formation of benzoic acid derivatives. The results were confirmed by comparisons of SERS spectra of para-substituted polystyrenes and benzoic acids.

Shindo investigated SERS from nitrobenzene adsorbed on a silver electrode (10). Trans-azobenzene and two unknown species with bands near 1152, 1245, 1350, and 1408 cm^{-1} were detected when the electrode was held at a potential of -0.5 V vs SCE. At -1.2 V, weakly adsorbed aniline, which was characterized by bands near 996 and 1025 cm^{-1} , became the dominant species on the electrode. Moreover, the orientation of the adsorbed species was characterized by changes in the intensities of the SERS bands. It was suggested that aniline was adsorbed with the aromatic rings parallel to the electrode surface. SERS from adsorbed aniline was also investigated at more cathodic potentials. When the potential was -0.6 V, the two unknown species with bands near 1157, 1245, 1338, and 1407 cm^{-1} were still detected on the electrode.

Roth, Venkatachalam, and Boerio studied SERS from thin films of p-nitrobenzoic acid (PNBA) adsorbed onto silver island films (11). At low laser powers (e.g., 5 mW), the SERS spectrum of PNBA was very similar to the normal Raman spectrum of the sodium salt of PNBA, indicating that PNBA was adsorbed as a metal salt. When PNBA films on the silver island films were irradiated at high laser powers, a band near 1460 cm^{-1} and a doublet near 1150 cm^{-1} due to azodibenzoate gradually appeared, indicating that PNBA was reduced to form azodibenzoate at the silver surface during intense laser irradiation.

Venkatachalam, Boerio, and Roth also investigated SERS from thin films of p-aminobenzoic acid (PABA) adsorbed onto silver island films (12). PABA was very reactive and easily formed azodibenzoate when exposed to a moist environment and laser light. However, this reaction was inhibited when samples were stored in a dry environment such as a dessicator prior to SERS experiments or maintained in a vacuum system during the experiments. It was concluded that two steps were associated with the mechanism of azodibenzoate formation from PABA. The first was hydrolysis of the amine while the second involved dimerization during laser exposure.

Since aromatic compounds containing nitro groups are easily reduced to aromatic azo compounds during SERS, it was considered that aromatic compounds containing two nitro groups might polymerize to form aromatic azo polymers at the silver surface during intense laser irradiation. In order to investigate this possibility, SERS from thin films of 1,4-dinitrobenzene (1,4-DNB)

and 1,3-dinitrobenzene (1,3-DNB) adsorbed onto silver island films were investigated. The results obtained showed that 1,4-DNB did polymerize but 1,3-DNB did not.

II. Experimental

Samples were prepared for SERS investigations as described below. Glass slides were cut into small pieces (1.2 cm x 1.2 cm) and etched in a mixture of chromic and sulfuric acids for several hours. The slides were then rinsed in distilled-deionized water, blown dry with nitrogen, cleaned ultrasonically in absolute ethanol for fifteen minutes, and blown dry with nitrogen again.

The glass slides were placed in a vacuum chamber (glass bell jar) which was purged with nitrogen and pumped down to 10^{-6} Torr using sorption, sublimation, and ion pumps. Then, 99.9% silver wire which was wrapped around a tungsten filament in the vacuum chamber was slowly heated to evaporate the island films onto the glass slides. For the best enhancement, the thickness of the silver island films was controlled at about 40 angstroms using a quartz crystal oscillator thickness monitor. The deposition rate, which affected the roughness, was controlled at approximately 1 angstrom per second.

1,4-DNB and 1,3-DNB were purchased from Aldrich Chemical Company and purified by recrystallization from ethanol before use. Thin films of 1,4-DNB and 1,3-DNB were deposited on the silver films by spin-coating from dilute solutions in reagent-grade acetone. In order to determine the thickness of organic films on the SERS samples, thick films of silver were evaporated

onto glass slides. Films of 1,4-DNB and 1,3-DNB were spin-coated onto the silver mirrors from the same solutions and at the same speeds as were used to prepare the SERS samples. The thicknesses of the 1,4-DNB and 1,3-DNB films were determined using a Rudolph Research Model 436 ellipsometer to examine the silver films before and after deposition of the organic films. It was found that 1,4-DNB films approximately 80 and 710 angstroms thick were deposited from 0.4% and 3.0% solutions, respectively.

Normal and surface-enhanced Raman spectra were obtained using a spectrometer equipped with a Spex 1401 double monochromator, an ITT FW130 photomultiplier tube, Harshaw photon counting electronics, and a Spectra-Physics Model 165 argon-ion laser. The monochromator was equipped with ruled gratings (1200 g/mm) which were blazed at 5000 angstroms and worked in the first order. The slits of the monochromator were set at 400 μm for the SERS spectra and at 200 μm for the normal spectra. These slit settings provided a spectral resolution of 10 cm^{-1} for the SERS spectra and 5 cm^{-1} for the normal Raman spectra. The green line (5145 angstroms in wavelength) was incident on the sample at an angle of about 65° relative to the normal of the sample surface for SERS experiments and was s-polarized. In a few cases, SERS spectra were obtained using a glass cell which was purged with N_2 . In obtaining the normal Raman spectra, a glass capillary tube was used to support a small amount of the sample powder.

Plasma lines were removed from the spectra by the placement of a narrow-bandpass filter between the laser and the sample. The scattered light was collected using an f/0.95 collection lens

and was focused onto the entrance slits of the monochromator. All of the spectra were obtained using a scan speed of 50 cm^{-1} per minute and a time constant of either 2 or 10 seconds.

III. Results and Discussion

The normal Raman spectrum of 1,4-DNB is shown in Figure 1. The strong bands near 1358 and 1372 cm^{-1} were assigned to the NO_2 symmetric stretching mode. Other characteristic bands near 877 and 776 cm^{-1} were assigned to an NO_2 symmetric deformation mode and to an NO_2 non-planar deformation mode, respectively. Most of the remaining bands observed in the normal Raman spectrum of 1,4-DNB were attributed to vibrations of the benzene ring and can be discussed in terms of Wilson's numbering system (13). Thus, the medium intensity band near 1118 cm^{-1} was assigned to $\nu(7a)$, a CN stretching mode. Other medium intensity bands near 1598 and 633 cm^{-1} were assigned to $\nu(8a)$, a tangential ring stretching mode, and to $n(6b)$, a radial ring stretching mode, respectively.

Several weak bands observed in the spectrum can also be assigned to ring modes. The bands near 1254 and 1015 cm^{-1} were assigned to the CH in-plane bending modes $\nu(3)$ and $\nu(18a)$, respectively. Bands observed near 1213 and 840 cm^{-1} were assigned to $\nu(14)$, a tangential ring stretching mode, and to $\nu(10a)$, a CH out-of-plane bending mode, respectively. The band near 452 cm^{-1} was attributed to $\nu(12)$, a radial ring stretching mode while the band near 435 cm^{-1} was related to $\nu(16a)$, an out-of-plane ring mode.

The SERS spectrum obtained in air from thin films of 1,4-DNB adsorbed onto silver island films using a laser power of 5 mW was

similar to the normal Raman spectrum of 1,4-DNB. However, the band associated with $\nu(8a)$, which was observed near 1598 cm^{-1} in normal Raman spectra of 1,4-DNB, shifted upward somewhat in frequency and a shoulder appeared near 1350 cm^{-1} .

In a series of experiments, thin films of 1,4-DNB were spin-coated onto silver island films from 0.4% solutions in acetone and irradiated in air at a laser power of 600 mW. At selected intervals, the laser power was reduced to 100 mW and the SERS spectrum of the 1,4-DNB was obtained while the samples were exposed to air. When the SERS spectrum was obtained without any irradiation at a laser power of 600 mW, $\nu(8a)$ again shifted from 1598 cm^{-1} to near 1605 cm^{-1} , new bands appeared near 1152, 1412, and 1460 cm^{-1} , and a shoulder appeared near 1350 cm^{-1} (see Figure 3A). Moreover, when the SERS spectrum was obtained following laser irradiation at 600 mW for 5 and 45 minutes (see Figures 3B and 3C, respectively), significant spectral changes were observed. A new band appeared near 1350 cm^{-1} and the intensities of the bands near 1152, 1412, and 1460 cm^{-1} increased while the intensities of the bands near 1118, 1358, and 1372 cm^{-1} decreased. It was also found that the intensity of the bands near 877, 1118, 1358, and 1372 cm^{-1} decreased relative to the band near 1605 cm^{-1} with increasing time of laser exposure but the intensity of the bands near 1152 and 1412 cm^{-1} increased.

As mentioned above, the concentration effect plays an important role in determining both molecular geometry and surface coverage (8). A series of experiments was carried out to determine the effect of concentration of solutions from which

1,4-DNB films were deposited on the spectral changes shown in Figure 3. The experimental conditions were the same as described above except that the concentration of the solutions from which the 1,4-DNB was spun onto silver island films was increased from 0.4% to 3%. As shown in Figure 4, the intensity of the bands near 1358, 1372, 1118 cm^{-1} , and 877 cm^{-1} again decreased relative to that of the band near 1605 cm^{-1} as exposure to the laser beam increased while that of the bands near 1152 and 1412 cm^{-1} increased. A strong band was also still observed near 1350 cm^{-1} .

In another series of experiments, SERS spectra were obtained from films of 1,4-DNB spin-coated onto silver island films from 3% solutions while the samples were held under a nitrogen atmosphere (see Figure 5). The intensity of the bands near 877, 1118, 1358 and 1372 cm^{-1} decreased relative to that of the band near 1605 cm^{-1} but the intensity of the bands near 1152 and 1412 cm^{-1} increased with increasing time of laser exposure. Moreover, the bands near 1358, 1372, 1118, and 877 cm^{-1} almost disappeared and the band near 1350 cm^{-1} that was so prominent in Figure 4C was almost not observed.

Raman spectra of azo dye structures have been analyzed by Trotter (14). A band related to the -N=N- stretching vibration appeared in the 1405-1450 cm^{-1} region while the CN (azo) symmetric stretching mode was observed in the 1130-1160 cm^{-1} region. Lorriaux et al also investigated para-substituted derivatives of azobenzene by resonance Raman spectroscopy (15). For most azo compounds, the $\phi\text{-N}$ mode was observed in the 1140-1150 cm^{-1} region while the -N=N- mode appeared in the 1400-1440

cm^{-1} region. Similar assignments of the $\phi\text{-N}$ and -N=N- modes were also reported by other investigators (16-18). Based on these reports, the new bands observed near 1152 and 1412 cm^{-1} in our spectra were tentatively assigned to phenyl-N and the -N=N- stretching modes of aromatic azo polymers, respectively. Azo is a well known group which is much photo-resisted. As mentioned before, the bands near 1152 and 1412 cm^{-1} were still observed following intense laser irradiation. This provides additional evidence for the assignment of these two bands.

As shown in Figures 3 and 4, decreases in the intensities of the bands near 1358 and 1372 cm^{-1} not only corresponded to increases in the intensity of the band near 1412 cm^{-1} but also to the appearance of the 1350 cm^{-1} band in the final stages of intense laser irradiation. However, this was not true for the spectra shown in Figure 5. The band near 1350 cm^{-1} was not observed in the spectra shown in Figure 5, and the decreases in the intensities of 1358 and 1372 cm^{-1} bands corresponded directly to the appearance of the band near 1412 cm^{-1} . Therefore, the band near 1350 cm^{-1} was believed to be related to an intermediate between a monomer (1,4-DNB) and an aromatic azo polymer during the SERS processes. Moreover, since the -N=N- stretching mode of the dimer (p-nitrophenyl azo compound) appears near 1463 cm^{-1} (19), it was suggested that the band observed near 1460 cm^{-1} was related to the -N=N- mode of low molecular weight species during this polymerization process.

As mentioned before, the band observed near 1605 cm^{-1} in the SERS spectrum of 1,4-DNB was attributed to the ring stretching

mode $\nu(8a)$. As a result, this band can be used as a reference band for measurements of relative intensity. The bands near 877, 1118, 1358 and 1372 cm^{-1} were associated with the nitro groups of monomers (1,4-DNB) while the bands near 1152 and 1412 cm^{-1} were related to azo groups of aromatic azo polymers. Therefore, results obtained in Figures 3 and 4 indicated that 1,4-DNB monomers were partly reduced to form aromatic azo polymers during intense laser irradiation. However, the strong band near 1350 cm^{-1} which was associated with an intermediate between a monomer and an aromatic azo polymer still appeared in the spectra shown in Figures 3C and 4C, so the extent of reduction was small when laser irradiation was carried out with the samples exposed to air. However, as shown in Figure 5, the band near 1350 cm^{-1} was barely observed when SERS was carried out in a nitrogen atmosphere on films deposited from solutions having high concentration and the decreases in the intensities of the bands near 1358 and 1372 cm^{-1} corresponded directly to the appearance of a band near 1412 cm^{-1} . Therefore, the 1,4-DNB films were mostly polymerized to form aromatic azo polymers during intense laser irradiation when SERS was carried out in a nitrogen atmosphere on films deposited from solutions having high concentrations.

Moskovits et al investigated SERS from a number of aromatic molecules adsorbed onto silver island films and observed spectral changes following laser irradiation that were interpreted as being due to molecular reorientation upon the surface (20). If the spectral changes observed following laser irradiation of 1,4-

DNB films on silver were just due to molecular reorientation upon the surface, there would be no difference between SERS spectra obtained in air and in nitrogen. However, when spectra obtained from 1,4-DNB films exposed to air were compared with those obtained from films that were deposited from solutions having the same concentration but exposed to nitrogen (see Figures 4C and 5C), significant differences were observed. Bands near 1350 and 1118 cm^{-1} were still observed in the spectra shown in Figure 4C but they were not observed in the spectra shown in Figure 5C. Therefore, reorientation of the adsorbed species was not considered to be a satisfactory explanation of our results. Instead, the spectral changes we observed were interpreted as being due to polymerization occurring at the silver surface during intense laser irradiation.

The results of these investigations can be summarized as shown in Figures 6 and 7. In Figure 6, the intensity of the band near 1118 cm^{-1} relative to that of the band near 1605 cm^{-1} is plotted against irradiation time at 600 mW. As indicated above, the band near 1118 cm^{-1} was related to the nitro groups of 1,4-DNB while that near 1605 cm^{-1} was associated with the ring mode $\nu(8a)$. As a result, the intensity of the band near 1118 cm^{-1} relative to that near 1605 cm^{-1} was used as an index of the extent of 1,4-DNB conversion. It was expected that the intensity ratios would decrease with increasing irradiation time at 600 mW regardless of the environment in which the SERS experiments were carried out and that was in fact observed (see Figures 6A, 6B, and 6C, respectively). The results obtained show that the

conversion of 1,4-DNB to aromatic azo polymers during SERS involved a laser-induced process.

It is evident from Figures 6A, 6E, and 6C that the extent of conversion of 1,4-DNB to azo polymers depends on the environment in which the SERS experiments are conducted and on the surface coverage. This was demonstrated by determining the change in relative intensity of the bands near 1118 and 1605 cm^{-1} after a fixed time of irradiation, 45 min (see Figure 6D). The change in relative intensity was greater when the SERS experiments were carried out in nitrogen than when carried out in air. When the experiments were carried out in the same environment, the change in relative intensity was greater when the coverage was greater. The reason for this phenomenon is not clear now, but it probably can be explained that the conversion reaction is a reduction and is favored by that highly reducing environments which result from decreased oxygen supply.

Since the band near 1350 cm^{-1} was associated with an intermediate between 1,4-DNB monomers and aromatic azo polymers, the greater extent of 1,4-DNB conversion did not necessarily mean that higher yield of aromatic azo polymers was produced. The products could have been dominated by intermediates. In order to investigate this possibility, a plot of the intensity of the band near 1412 cm^{-1} relative to that of the band near 1605 cm^{-1} vs irradiation time at 600 mW was prepared (see Figure 7). As mentioned before, the band near 1412 cm^{-1} was related to aromatic azo polymers while the band near 1605 cm^{-1} was associated with the benzene rings. Therefore, this intensity ratio indicated

directly the yield of aromatic azo polymers. As shown in Figures 7A, 7B, and 7C, the intensity of the band near 1412 cm^{-1} relative to that of the band near 1605 cm^{-1} increased with increasing irradiation time at 600 mW for all three experimental conditions, indicating that formation of aromatic azo polymers involved a laser-induced process.

In order to determine the effect of coverage and environment on the extent of polymer formation, the change in relative intensity of the bands near 1412 and 1605 cm^{-1} after a fixed time of irradiation, 45 min, was determined (see Figure 7D). The change in relative intensity increased with increasing surface coverage of 1,4-DNB when the experiments were carried out in a fixed environment or when the reducing character of the environment was increased at a fixed coverage by conducting the experiments in a nitrogen-filled cell. Therefore, it was concluded that surface coverage and reducing environments were both important to determine the yield of aromatic azo polymers.

In a final series of experiments, we investigated the silver-catalyzed, laser-induced polymerization of 1,3-DNB during SERS. The normal Raman spectrum of 1,3-DNB is shown in Figure 8. The strong band near 1360 cm^{-1} was assigned to an NO_2 symmetric stretching mode. Another characteristic band near 1549 cm^{-1} was attributed to an NO_2 asymmetric stretching mode. The medium intensity band near 848 cm^{-1} was assigned to a symmetric deformation mode. Weak bands near 772 and 523 cm^{-1} were related to NO_2 non-planar and asymmetric deformation modes, respectively.

Most of remaining bands observed in the normal Raman spectrum of 1,3-DNB were attributed to the benzene ring vibrations and can again be discussed in terms of Wilson's numbering system (13). The medium band near 1610 cm^{-1} was assigned to $\nu(8b)$, a tangential ring stretching mode, while another medium band near 1156 cm^{-1} was related to $\nu(13)$, a CN stretching mode. Other medium bands near 1010 and 660 cm^{-1} were assigned to $\nu(12)$, a radial ring stretching mode, and to $\nu(1)$, another radial ring stretching mode, respectively. The weak intensity band near 1451 cm^{-1} was assigned to $\nu(19a)$, a tangential ring stretching mode. Other weak bands near 1180 and 915 cm^{-1} were attributed to ring modes $\nu(9b)$ and $\nu(17b)$, respectively.

1,3-DNB films were spin-coated onto silver island films from 3% solutions in acetone and irradiated at a laser power of 600 mW in air. At predetermined intervals, the laser power was reduced to 100 mW and the SERS spectrum was obtained. As shown in Figure 9A, the SERS spectrum obtained from 1,3-DNB prior to intense laser irradiation was similar to its normal Raman spectrum. Moreover, when the SERS spectra were obtained following laser irradiation at 600 mW for 5 and 15 minutes (see Figures 9B and 9C), no significant spectral changes were observed except that thermal desorption occurred. These results are considerably different from those obtained for 1,4-DNB which reacted readily to form azo polymers during intense laser irradiation.

There are two possible explanations for the failure of 1,3-DNB to react at the silver surface during intense laser

irradiation. One is related to electron withdrawal from the substituents on the benzene ring. The other is related to the orientation of adsorbed species with respect to the metal surface.

Bunding reported SERS from 4- and 3-pyridine-carboxaldehyde (PCA) adsorbed onto silver electrodes (21). It was found that 4-PCA interacted with water to form 4-pyridylcarbinol at the surface but 3-PCA did not. The results were explained by the interaction of the nitrogen lone-pair electrons. As a result, a chemisorbed bond would lead to electron withdrawal from the 4-substituent but not from the 3-substituent. Boerio et al reported similar results when they investigated SERS from thin films of p- and m-nitrobenzoic acid (NBA) adsorbed onto silver island films (11, 22). It was found that PNBA was reduced to form azodibenzoate at the silver surface during intense laser irradiation but MNBA was not. This can be explained by the interaction of -COOH group with silver causing electron withdrawal from the p-substituent but not from the m-substituent. In dinitrobenzene, both substituents are electron-withdrawing groups, so the explanation described before is not suitable for our case.

It may be speculated that silver-catalyzed polymerization takes place only when dinitrobenzene is adsorbed onto the silver surface with the aromatic rings parallel to the surface. In that case, both NO₂ groups can interact with the silver surface and react. Unfortunately, it is difficult to determine the molecular orientation of 1,4-DNB and 1,3-DNB with respect to the silver

surfaces from the SERS spectra since the out-of-plane CH bending modes are much weaker in Raman scattering than the in-plane modes. However, it is well known that 1,3-DNB can be reduced to form m-nitroaniline (MNA) in catalytic reactions (23). This reaction can be explained if only one NO₂ group of 1,3-DNB is adsorbed onto the metal surface and reduced to form MNA. It may be that a similar effect occurred in the case of the SERS experiments. That is, 1,3-DNB was adsorbed onto the silver surface with a vertical conformation in which the aromatic rings were perpendicular to the surface and one NO₂ group was in contact with the surface. As a result, the NO₂ group adjacent to the metal surface was catalyzed to form an NH₂ group.

Considering that 1,4-DNB did undergo polymerization during SERS while 1,3-DNB did not, it may be speculated that 1,4-DNB was adsorbed with both NO₂ groups attached to the silver surface and the aromatic rings parallel to the surface. However, further investigations are necessary to substantiate this conclusion.

IV. Conclusions

The results obtained here showed that 1,4-dinitrobenzene films adsorbed onto silver island films polymerized during intense laser irradiation in surface-enhanced Raman scattering experiments. High surface coverages and highly reducing environments were both required to obtain high yields of aromatic azo polymers. Polymerization did not occur in bulk 1,4-DNB even when high laser powers were applied. Therefore, it was concluded that polymerization occurring during SERS involved a silver-catalyzed, laser-induced process.

No azo compounds were formed during intense laser irradiation of 1,3-DNB adsorbed onto silver island films. These results may be explained by different configurations of adsorbed 1,3-DNB and 1,4-DNB with respect to the silver surface. It was speculated that 1,4-DNB was adsorbed through both NO₂ groups and with the aromatic rings parallel to the surface while 1,3-DNB was adsorbed through just one NO₂ group and with the aromatic rings perpendicular to the surface. Thus, the orientation of the adsorbed species with respect to the metal surface was also important for the polymerization to occur. However, much fundamental work is necessary to understand this phenomenon.

V. Acknowledgements

This research was supported in part by grants from the Office of Naval Research and the National Science Foundation Polymers Program. The assistance of Kristen A. Boerio in preparing the figures is also acknowledged.

VI. References

1. Jeanmaire, D. J., and R. P. Van Duyne, J. Electroanal. Chem. 84, 1 (1977).
2. Metiu, H., in Surface-Enhanced Raman Scattering, R. K. Chang and T. E. Furtak, eds., Plenum Press (New York), 1982, p. 1.
3. Dorain, P. B., Von Raben, K. U., Chang, R. K., and B. L. Laube, Chem. Phys. Lett. 84, 405 (1981).
4. Boerio, F. J., Tsai, W. H., and G. Montaudo, J. Polymer Sci., Part B: Polymer Phys. 27, 1017 (1989).
5. Von Raben, K. U., Dorain, P. B., Chen, T. T., and R. K. Chang, Chem. Phys. Lett. 95, 269 (1983).
6. Wokaun, A., and A. Baiker, Chimia 40, 2 (1986).
7. Suh, J. S., and K. H. Michaelian, J. Raman Spectrosc. 18, 408 (1987).
8. Suh, J. S., and K. H. Michaelian, J. Phys. Chem. 91, 598 (1987).
9. Boerio, F. J., Tsai, W. H., Hong, P. P., and G. Montaudo Macromolecules, accepted for publication, 1989.
10. H. Shindo, J. Chem. Soc., Faraday Trans. I 82, 45 (1986).
11. Roth, P. G., Venkatachalam, R. S., and F. J. Boerio, J. Chem. Phys. 85, 1150 (1986).
12. Venkatachalam, R. S., Boerio, F. J., and P. G. Roth, J. Raman Spectrosc. 19, 281 (1988).
13. Varsanyi, G., Vibrational Spectra of Benzene Derivatives Academic Press (New York), 1969.
14. Trotter, P. J., Appl. Spectrosc. 31, 30 (1977).
15. Lorriaux, J. L., Merlin, J. C., Dupaix, A., and E. W. Thomas, J. Raman Spectrosc. 8, 81 (1979).
16. Isono, N., Umemura, T., Takenaka, T., Shimomura, M., and T. Kunitake, J. Colloid Interface Sci. 117, 400 (1987).
17. Ni, F., and T. M. Cotton, J. Raman Spectrosc. 19, 429 (1988).
18. Tian, Y., Umemura, T., and T. Takenaka, Langmuir 4, 1064 (1988).
19. Colthup, N. B., Daly, L. H., and S. E. Wiberley,

Introduction to Infrared and Raman Spectroscopy, 2nd ed.
Academic Press (New York), 1975, p. 331.

20. Moskovits, M., DiLella, D. P., and K. J. Maynard, *Langmuir* 4, 67 (1988).
21. K. A. Bunding, Ph.D. Dissertation, City University of New York (1980).
22. Venkatachalam, R. S., and F. J. Boerio, unpublished results.
23. Norman, R. O. C., Principles of Organic Synthesis, 2nd ed., Chapman and Hall (London), 1978, p. 649.

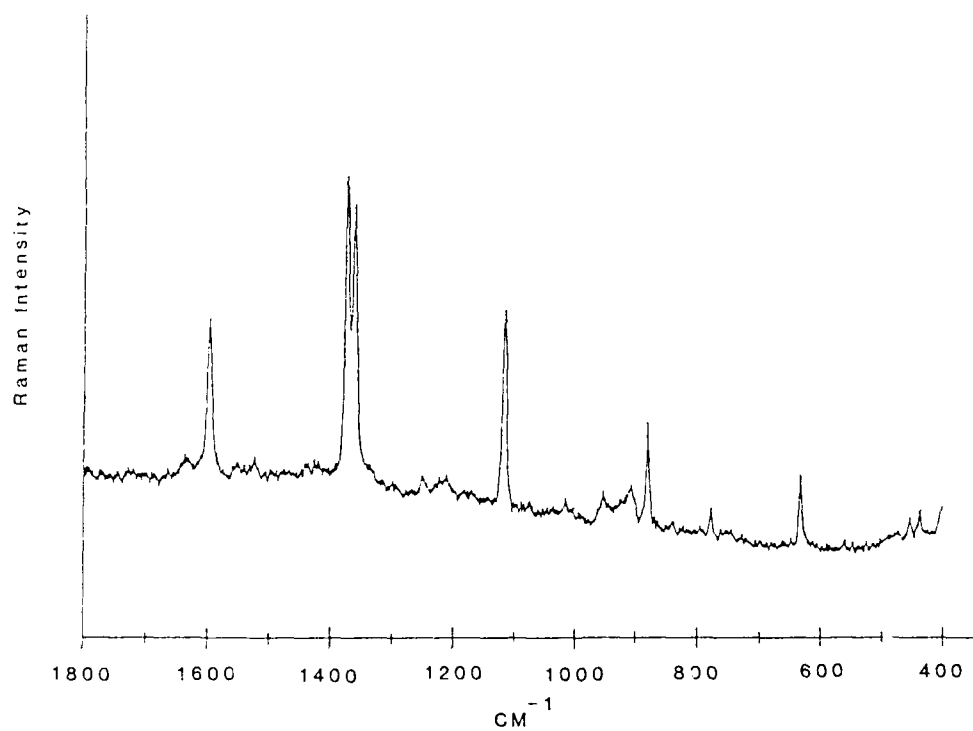


Figure 1. Normal Raman spectrum of 1,4-dinitrobenzene.

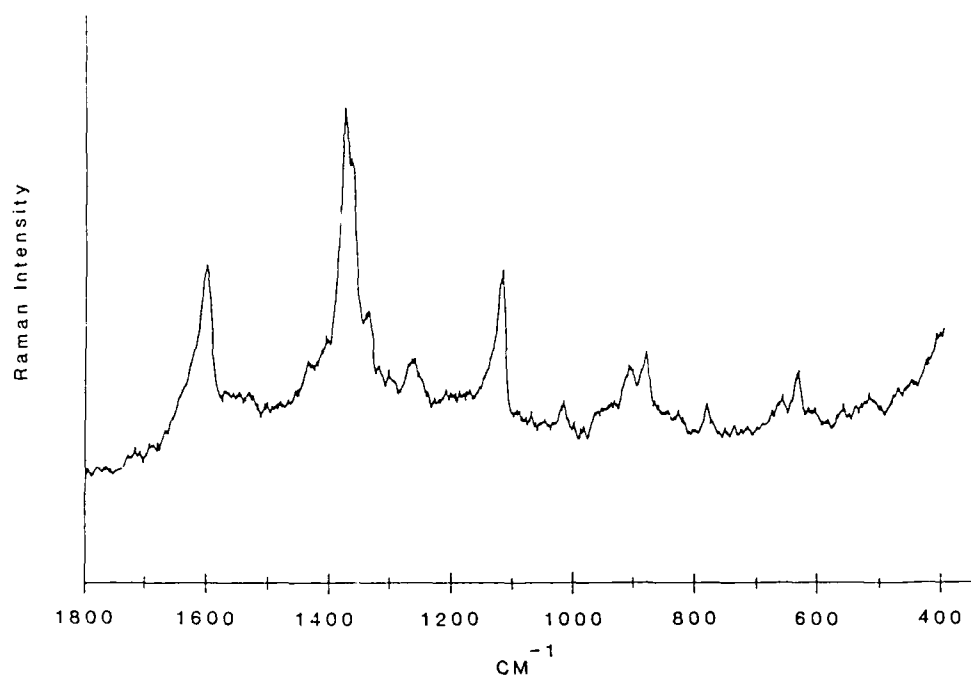


Figure 2. Surface-enhanced Raman spectrum of 1,4-dinitrobenzene spin-coated onto a silver island film from a 3% solution in acetone. The SERS experiments were carried out in air using a laser power of 5 mW.

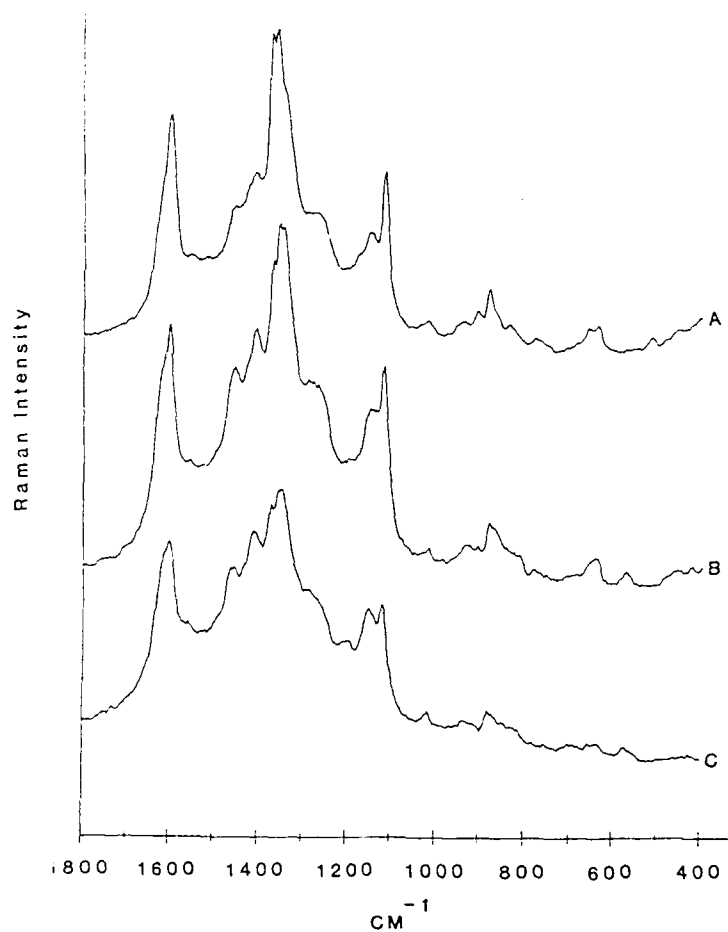


Figure 3. SERS spectra obtained from films of 1,4-DNB spin-coated onto a silver island film from a 0.4% solution in acetone. The spectra were obtained with the samples exposed to air and with a laser power of 5mW after the samples were irradiated with the laser at 600 mW for (A)-0, (B)-5, and (C)-45 minutes.

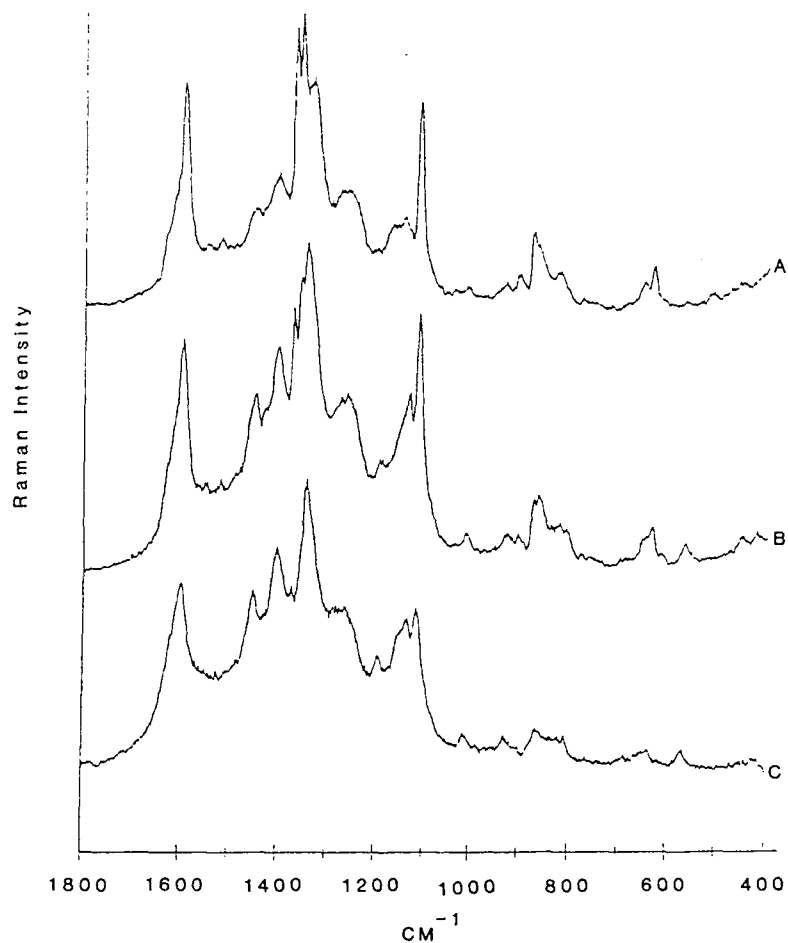


Figure 4. SERS spectra obtained from films of 1,4-DNB spin-coated onto a silver island film from a 3.0% solution in acetone. The spectra were obtained with the samples exposed to air and with a laser power of 5mW after the samples were irradiated with the laser at 600 mW for (A)-0, (B)-5, and (C)-45 minutes.

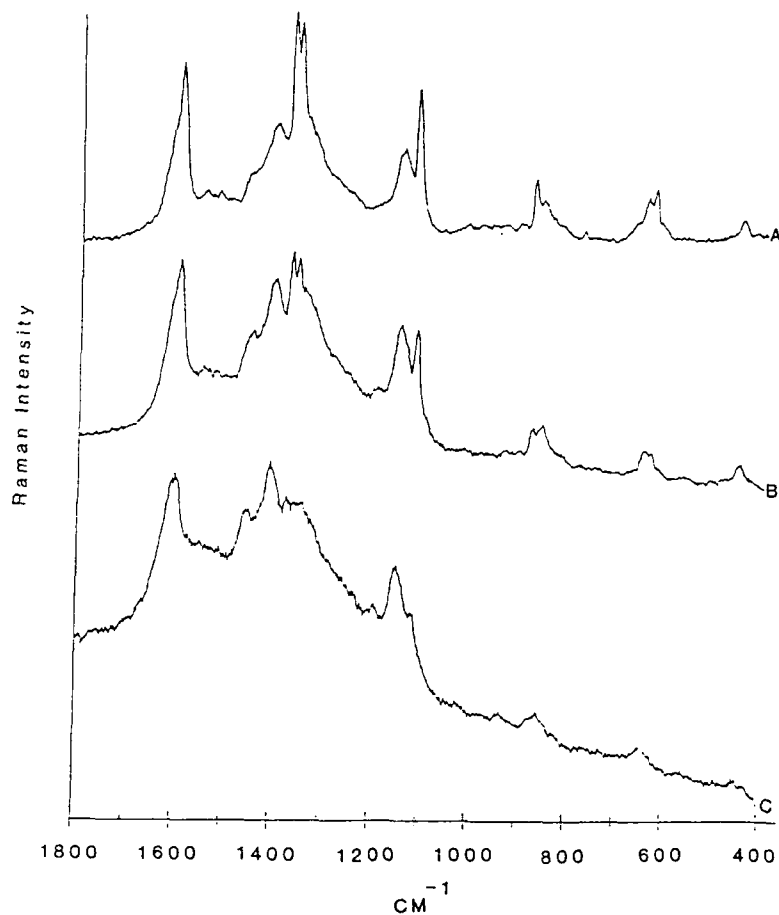


Figure 5. SERS spectra obtained from films of 1,4-DNB spin-coated onto a silver island film from a 3.0% solution in acetone. The spectra were obtained with the samples exposed to nitrogen and with a laser power of 5mW after the samples were irradiated with the laser at 600 mW for (A)-0, (B)-5, and (C)-45 minutes.

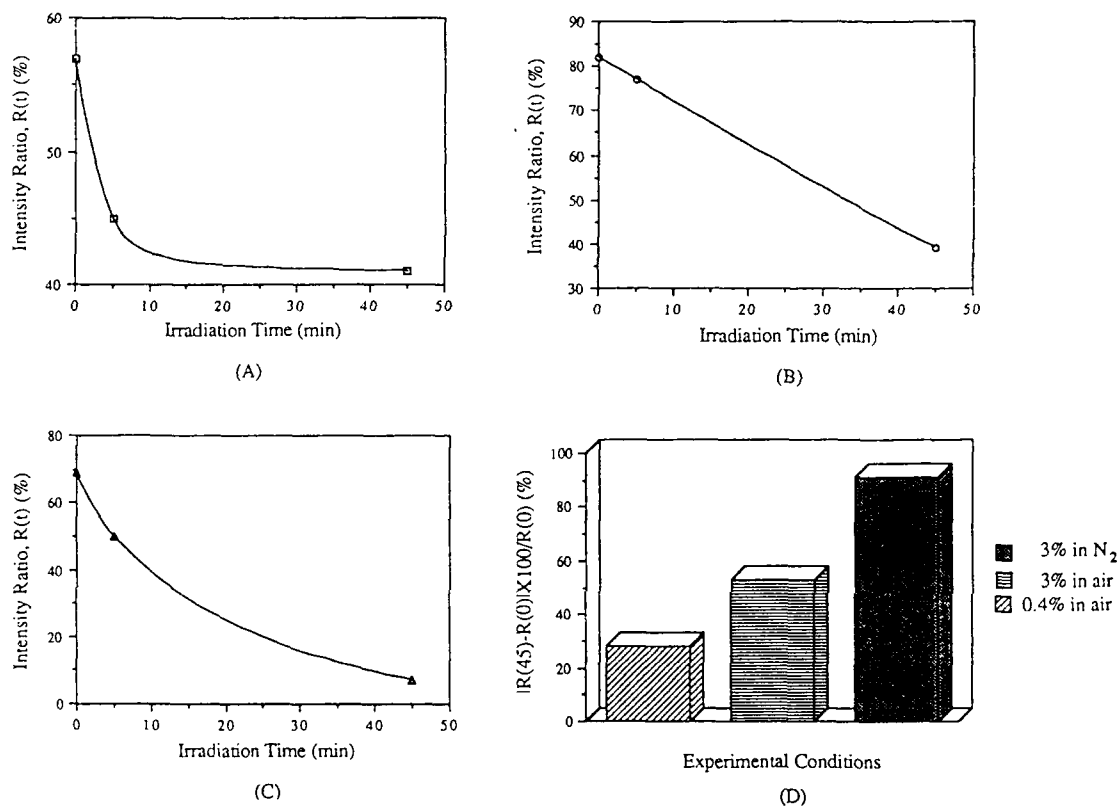


Figure 6. Relative intensities of the bands near 1118 and 1605 cm^{-1} in the SERS spectra of 1,4-DNB as a function of time of irradiation at a laser power of 600 mW. In A, the 1,4-DNB films were deposited from 0.4% solutions and the SERS experiments were carried out in air. In B, the films were deposited from 3% solutions and the SERS experiments were conducted in air. In C, the films were deposited from a 3% solution and the experiments were carried out in nitrogen. In D, the change in relative intensity of the bands is shown after 45 min irradiation for the same experimental conditions.

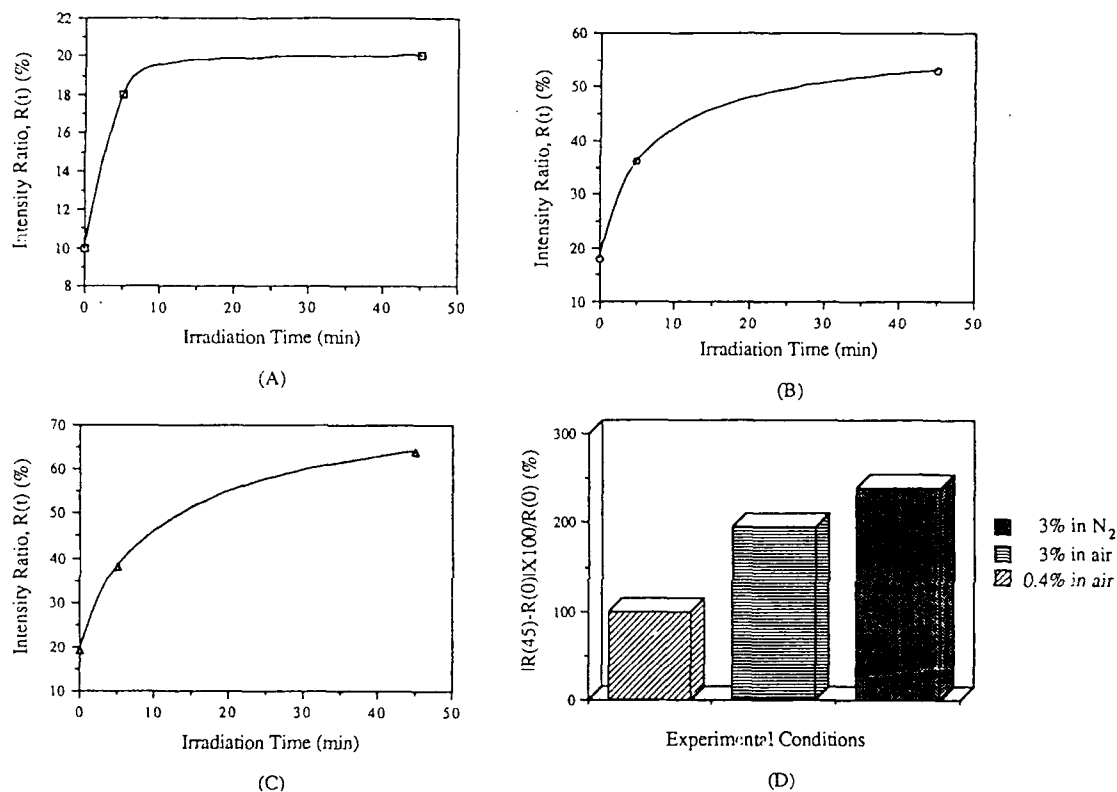


Figure 7. Relative intensities of the bands near 1412 cm^{-1} in the SERS spectra of 1,4-DNB as a function of time of irradiation at a laser power of 600 mW. In A, the 1,4-DNB films were deposited from 0.4% solutions and the SERS experiments were carried out in air. In B, the films were deposited from 3% solutions and the SERS experiments were conducted in air. In C, the films were deposited from a 3% solution and the experiments were carried out in nitrogen. In D, the change in relative intensity of the bands is shown after 45 min irradiation for the same experimental conditions.

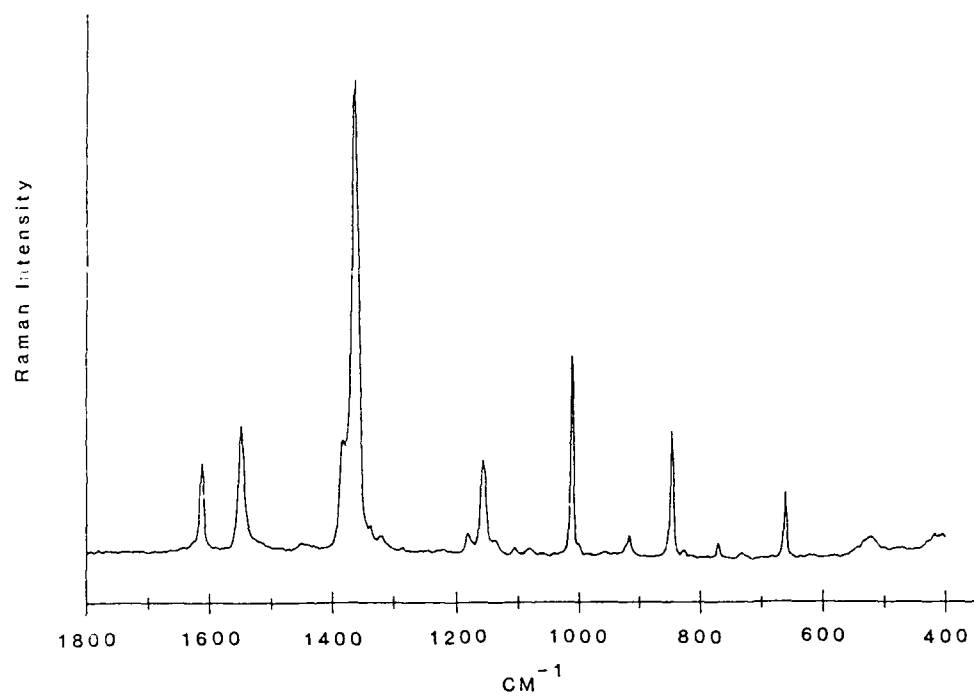


Figure 8. Normal Raman spectrum of 1,3-dinitrobenzene.

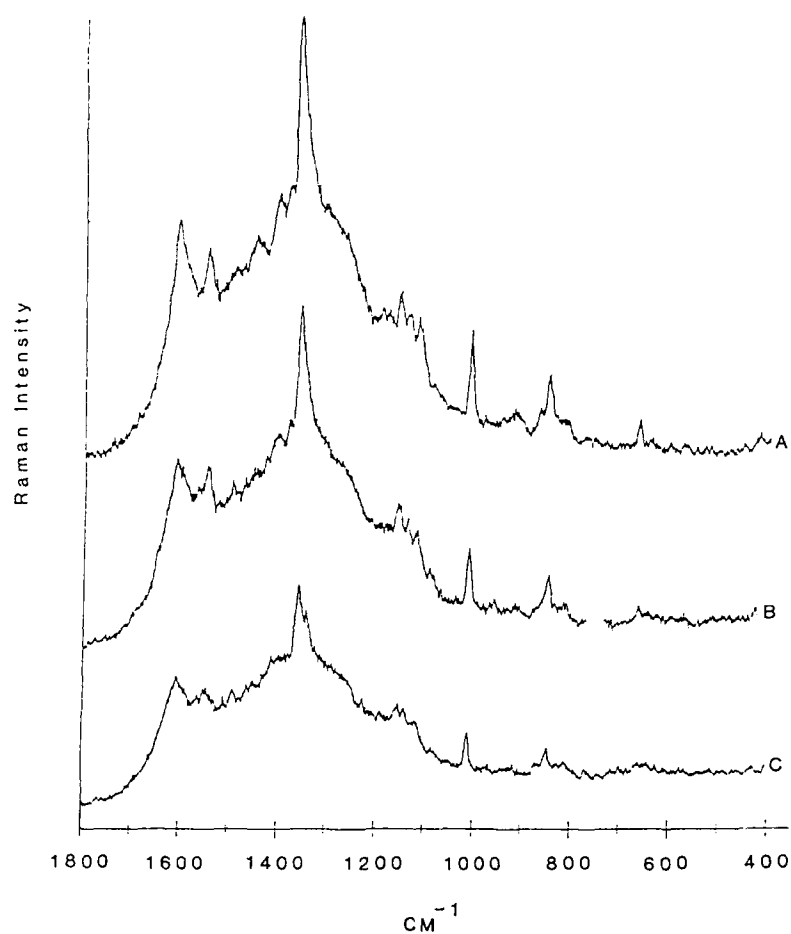


Figure 9. SERS spectra obtained from films of 1,3-DNB spin-coated onto a silver island film from a 3.0% solution in acetone. The spectra were obtained with the samples exposed to air and with a laser power of 5mW after the samples were irradiated with the laser at 600 mW for (A)-0, (B)-5, and (C)-15 minutes.

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